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DEVELOPMENT OF ULTRA-THIN FILM
PRESERVATIVE COMPOUNDS

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6 June 1961 through 30 Sept. 1961

FOSTER D. SNELL, INC.

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FOR

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FOSTER D. SNELL, INC.
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ABSTRACT

A survey of the literature on corrosion and its control has been completed. Literature surveyed indicated no compounds currently in use which are being employed as ultra-thin film preservative compounds.

Construction of a controlled cyclic condensation humidity cabinet was started.

I. INTRODUCTION

Most metals represent a high-energy state with respect to their ores and, consequently, should revert to this state with release of energy unless energy from some external source is expended in maintaining the metallic state. Essentially corrosion control is the prevention of the reaction of a metal with its environment to form products at a lower energy level. Methods of reducing corrosion involve one or more of the following: ¹

- (1) purification of metals
- (2) alloying
- (3) additions to the environment (inhibitors)
- (4) alteration of the environment
- (5) galvanic protection (cladding and external sacrificial protection).
- (6) surface coatings on the metal (oxide and other chemical conversion films, metal-plating, and painting).

Metal preservative compounds usually effect control of corrosion as an addition to the environment or as a surface coating on the metal (methods 3 and 6). Use of preservative compounds to control corrosion is, perhaps, the cheapest and most widely adaptable way of preventing metallic corrosion. However, presently available preservative compounds cannot be used on many metal surfaces where protection is

necessary, for the following reasons:

(1) They interfere with the normal operation of most parts or equipment, and must be completely removed prior to installation or utilization. (This removal is not always practicable).

(2) The time required to effect complete removal of normal preservatives is an obstacle in the maintenance of those parts and equipment, which, ideally, should be kept in a state of readiness.

(3) They destroy lubricating properties of dry film lubricants used in the operation of high-temperature bearings.

(4) They do not dry completely, and tend to accumulate dirt and dust particles upon exposure to atmosphere.

(5) They constitute a fire hazard by supporting combustion and contributing to flame propagation.

(6) They are often difficult to remove from riveted seams, faying surfaces and complex shapes.

(7) They interfere with visual inspection of parts and early detection of defects.

A preservative compound which would overcome the defects mentioned should be an ultra-thin, non-tacky, transparent film. It is the object of this research to develop such a preservative compound which will 1) afford a high degree of protection to metal surfaces 2) will not interfere with normal or dry-film lubrication and 3) will be applicable from quick-drying, non-toxic solvents.

It is probable that successful corrosion control from an ultra-thin film as described above will depend on both inhibitive and barrier properties. Inhibitors are defined as substances which, when added in small amounts to the environment, effectively decrease the corrosion rate. Since the corrosion rate is proportional to the current flow in a corrosion cell, which, in turn is dependent on the open-circuit potential, cathode and anode polarization, and resistance of the cell, an inhibitor is effective if it 1) decreases the open-circuit potential (passivation), 2) increases polarization (anodic or cathodic) or 3) increases the resistance of the cell. Inhibition has been variously attributed to adsorption, the formation of insoluble films at the point of attack, diffusion and concentration polarization effects, and to electron interaction between the inhibitor and atoms at the surface of the metal or alloy.

Metal coatings may act in two ways to protect metals from corrosion. They may isolate the metal surface from its environment by a relatively impervious film or they may provide protection by controlled release of an inhibitor from the film. Besides metal plating (which is a method of galvanic protection), metal coatings are generally of two types; chemical conversion coatings and organic coatings. Chemical conversion coatings may be metal oxides, metal oxides impregnated with corrosion inhibitors, insoluble and impervious films other than metal oxides such as phosphates and sulfates. Organic coatings used to protect metals may be

generally classified by the way in which they protect the metal from attack; as simple barrier coatings or as inhibitive coatings such as commercial red lead primer. Effectiveness of barrier films depends on mechanically isolating a metal from its environment and, therefore, on the continuity and impermeability of the film. Continuity and impermeability in turn depend on adhesion of the film to the metal surface, cohesion between molecules of the film, and stability of the film with respect to age and environmental conditions.

The problem of developing preservative compounds which function efficiently as an ultra-thin film depends on method of application as well as selection of materials. Methods of application include, but are not limited to:

- (1) application from dilute solution
- (2) adsorption (of polar compounds) from non-polar solvents
- (3) exposure to surface-reactive vapors
- (4) vacuum deposition

It is our intention to concentrate our initial search on compounds which can be applied by methods 1) and 2), since these methods have more universal applicability.

The initial search for materials will be conducted among currently known preservative ingredients and compounds. These would include such materials as:

- (1) monocarboxylic acids and their salts
- (2) salts of sulfonic acids
- (3) salts of phosphoric acid derivatives
- (4) esters of carboxylic, phosphoric and sulfonic acids
- (5) ammonium and amine compounds of 1), 2), 3) and 4)
- (6) amine nitrites
- (7) pentaerythritol monoesters, glyoxalidines, highly fluorinated acids and their derivatives
- (8) resinous and polymeric film formers
- (9) waxes
- (10) metal oxides (as applied from esters of these oxides)
- (11) grade 3 compounds of MIL-C-16173A

This list is, of course, not exclusive, nor does it pretend to be inclusive of the currently known preservative materials. Materials will be evaluated for corrosion prevention in the application envisaged (ultra-thin films of less than .0005 inches) in multi-component compounds as well as single compounds.

The first phase of this investigation has consisted primarily of a search of the literature concerning methods of testing, materials and means of application of possible interest to the solution of this problem.

II. CORROSION TEST METHODS

A. GENERAL

While it is true that the final judgement of a material's ability to protect metal from corrosion is based on performance of the material in actual service, in-service testing is an excessively time-consuming and awkwardly expensive tool for use in research and development of corrosion control materials. In-service tests of materials find their primary utility is limited by economic considerations to post-development correlation of laboratory test data. Accelerated laboratory tests are intended to provide data in a short time which can be correlated to long-term normal use conditions. However, there is always the danger that the conditions of acceleration may have an unrealistic influence on the test system and provide questionable results. Nevertheless, it is imperative that some accelerated test procedure be used in order to screen the few most likely materials from among the many possible one for the intended application, or the task would probably become hopelessly time-tangled. Experience enables us to learn which test procedures are most suited to given needs. In order to understand better the usefulness and limitations of corrosion tests, they may be classified according to their principal objectives. The objectives of a corrosion test may be one or more of the following: ²

- (1) Study the corrosion mechanism and factors which influence it.
- (2) Select the best material or coating to withstand a particular corrosive environment.
- (3) Determine the environments which a given material withstands.
- (4) Develop materials for particular uses.
- (5) Study the effectiveness of various protective measures.
- (6) Control product uniformity in the manufacture of corrosion resistant materials.

In our present study, a principal objective of the test method (or methods) is the selection of a material (or materials) which, when applied as an ultra-thin film on bare metals, affords protection from corrosion likely to be encountered in normal storage environments.

It would be economically and physically impracticable to include, in one test, all of the variable conditions which might be encountered in the many possible actual storage environments. When it can be established that a given factor is not a significant cause of failure in the particular conditions under consideration, then consideration of that factor can be omitted from the test. In most partially shielded storage environments, the factors which are of greatest importance in their influence on corrosion are temperature, humidity and air content.

Air content will vary from location to location and attempts to regulate this factor in a laboratory test might provide misleading data. It might be feasible to consider this factor in supplementary tests after general screening to provide additional data for specific circumstances.

Humidity and temperature affects on corrosion are common to a greater or lesser degree to all environments. It is not too difficult to exercise control of these factors in laboratory tests and there are many corrosion tests which are based on these effects in current use. Most of these tests, however, do not allow for the heterogeneous nature of effects of environment and materials at varying conditions of humidity and temperature. That is, the relative order of attack upon different materials seldom remains constant at various conditions of humidity and temperature. Some materials may appear more resistant at increased humidity (and/or temperature) than would be expected from the behavior of these materials in relation to other materials at a condition of lower humidity. Hence, there has been limited correlation between service performance of materials and data obtained in laboratory corrosion tests. A test method in which the test environment consists of cyclic conditions of humidity and temperature would simulate conditions prevailing in actual storage much more nearly than do most of the tests commonly used. Such a test should provide better predictability concerning the efficacy of materials for use in this application.

B. LABORATORY TEST METHODS

Immersion tests have been popular in laboratory testing. Various types of total, partial, and intermittent immersions apparatus have been

used for accelerated testing. Corrosive media range from distilled water to various acid, base or salt solutions. All of these tests are quite empirical and may bear little relationship to conditions of actual service. Their principal use is for routine checking of materials on a mass production basis.

In spray tests, such as the salt spray test, specimens are exposed to a fine spray or mist of the corrosive media in a closed chamber usually at a constant temperature. Fog particles settling on the specimens constantly replenish the corrosive solution. These tests have been used with many modifications, such as intermittent operation and different corrosive solutions, with varying degrees of success. However, reproducibility and correlation of results are ever present difficulties with this type of test. Despite the acknowledged lack of correlation and reproducibility of most of these tests, many, such as the salt spray, are still widely employed as arbitrary performance standards in both government and industrial specifications.

Controlled atmospheres created in many different types of apparatus are used in laboratory tests to simulate corrosive conditions provided by gas mixtures at various relative humidities. One of the widely used tests of this type is that described in Federal Specification JAN-H-792. In this test specimens are exposed to a continuous relative humidity of 100% at 120°F for a Specified period of time.

Other controlled atmosphere tests, allow for alternate wet and dry conditions on the specimens. K.G. Compton³ has suggested for an accelerated test, steady conditions at 49°C and 95% relative humidity periodically interrupted by chilling to 41°C to give condensation. Another method, which is similar to that just mentioned, suggests lowering the temperature from 120°F (49°C) to 80°F (27°C) over a period of about 60 minutes and returning to the higher temperature in 30 minutes.⁴ The relative humidity at the higher temperature should be over 90% in order that specimen surfaces retain condensed moisture for at least 2 hours. A full cycle for this test is completed in 12 hours.

There have been many other controlled atmosphere tests devised by various investigators but those mentioned are representative of the great majority of the tests in current use. F.F. Fowle⁵ used an 8-hour cycle of warm, moist air (1-1/2 hours), air containing the smoke from burning bituminous coal (3 hours), a fine water spray (1/2 hour), and warm dry air (3 hours), and obtained corrosion qualitatively similar to that observed in industrial and urban atmospheres. This test and some of the more highly refined controlled atmosphere tests present problems of control and economy of operation that make them impractical for most laboratories to consider.

Concerning the JAN-H-792 humidity cabinet test, there has been a notable lack of reproducible results as well as lack of correlation with field tests. The principal reason for lack of reproducibility has been

attributed to the lack of uniform moisture condensation on the steel test surface. A controlled moisture condensation apparatus was devised by H. Roden⁶ (described in ASTM Bulletin of July 1957 pp. 55-61) which offers somewhat greater reproducibility of results than does the humidity cabinet. However, the controlled condensation apparatus embodies the basic concept of the JAN-H-792 cabinet and represents a refinement in obtaining more reproducible results. One could not, therefore, expect any better correlation with field tests with this apparatus than with the JAN-H-792 cabinet. In fact, there is very good correlation of results with the older humidity cabinet, hence (although there is no supporting data) one might assume that the same lack of correlation should exist with field tests as had previously been the case. One very probable reason for the lack of correlation of accelerated tests, such as these with field tests, is that they expose the specimen to conditions of high temperature and high relative humidity (or, in this case, continual condensation or 100% R. H.) simultaneously. Conditions of high temperature and high relative humidity are rarely encountered in actual storage environments.

⁷
Minuti has developed a controlled cyclic condensation humidity cabinet which can reproduce cyclic condensation and evaporation conditions on the test specimens much more closely simulating actual conditions than the accelerated tests previously discussed. This cabinet incorporates features which provide for positive control of ambient conditions (temperature and humidity of the air) and positive control of specimen temperature thus producing uniform moisture concentration and a uniform condition for

condensation and evaporation. Ambient conditions in the cabinet can be controlled over a temperature range of 70° to 180° F at 25% to 95% relative humidity. Condensation on the test surface is accomplished by mounting specimens on water-tight specimen holders containing a water bath which can be periodically chilled below the dew point of the test atmosphere.

The principle of basing an accelerated laboratory corrosion test on varying conditions of ambient temperature and humidity and condensation and evaporation from test specimens has been recognized by many investigators in the field of corrosion control. Most of the tests surveyed in the literature which embody this principle fail to meet the criteria of a generally useful research and development tool in study of corrosion and corrosion control because they involve complex and cumbersome operations, lack positive control, are prohibitively costly in operation or construction, and often fail to yield reproducible results. The cabinet developed by Minuti seems, to a remarkable extent, to eliminate these disadvantages. Although only limited tests have been conducted with this new cabinet the results indicate an excellent degree of consistency and reproducibility of this type of test. While the construction of this cabinet may be somewhat more costly than a JAN-H-792 cabinet, the versatility of operation and greater validity of results and, consequently greater usefulness of this cabinet would seem to far outweigh its higher cost.

CONSTRUCTION OF CONTROLLED CYCLIC
CONDENSATION HUMIDITY CABINET

Details and drawings covering the construction of the controlled cyclic condensation humidity cabinet are presented in Report No. NAMC-AML 1170 dated 27 December 1960 of the Aeronautical Materials Laboratory, Naval Air Material Center, Philadelphia, Pennsylvania. The cabinet being constructed for use in this laboratory is identical with the prototype cabinet except for the specimen holding trays. In the original cabinet, provision was made for accommodation of 9 specimen holders, each holder capable of mounting one 6" X 6" test specimen. In order to permit greater numbers of samples to be tested in the same amount of time, a modification has been made so that the cabinet will accommodate 5 specimen holders designed to be fitted with 10 test specimen mountings. Test specimens have an area dimension of 2" X 4". Detailed drawings of the modified specimen trays are presented in plate I.

IV. CORROSION PREVENTIVE MATERIALS

A survey of current corrosion literature and patents has indicated a lack of real information concerning the effectiveness of ultra-thin (0.5 mils or less thickness) films as preservative coatings. Most preservative compounds cited in the literature and patents may be classified as inhibited fluids and greases. While solid and semi-solid preservative coatings and films are, likewise, abundantly cited in current literature, these films are of much greater thickness than is contemplated in this project. Patents and articles describing "thin-film" rust preventive compounds refer to "thin-films" on the order of 1 to 5 mils thickness. Except for metal and metal-oxide coatings deposited on metal surfaces by electrochemical or vapor-deposition techniques, corrosion preventive films of 0.5 mils (or less) thickness appear nowhere in the literature.

Despite the lack of mention of compounds specifically related to our current effort, several encouraging bits of information have been noted. In a long term field test, "Teflon" films 0.6 to 1.0 mil thick were observed to protect internal metal surfaces from rusting. The metal appeared to be protected from rusting even after the "Teflon" film had worn away or been otherwise damaged.⁸

In another study, inclusion of small amounts of small amounts (2% to 5%) of organotitanates in siloxane and zinc chromate primer formulations were reported to increase the adhesion of these coatings to magnesium alloy surfaces.⁹

While Teflon films are able to protect internal metal surfaces from rusting, protection against rusting on external metal surfaces was borderline or inferior. In addition, there is no known room temperature solvent for "Teflon".

Since the ability of organic coatings to protect metal surfaces from corrosive attack depends in some degree on adhesion of the coating to the metal surface, improvement in adhesion of many organic substances, heretofore ineffective as corrosion control agents, may have a salutary effect on their ability to protect metals from attack. In this respect, titanium esters may offer an interesting key to the development of effective rust preventing "ultra-thin" films.

Perhaps, the most important reason for the absence of solution applied ultra-thin films for corrosion prevention from literature and patents is that little effort (or at any rate, little reported effort) has been expended in the development of this type of material. If this is the case, a likely explanation might be that application of films from dilute solutions represents, in general, low economy for both user and maker of such products.

SUMMARY

A survey of the literature revealed a widespread dissatisfaction with current accelerated laboratory corrosion tests. Despite the general dissatisfaction with many of the commonly used test methods such as the JAN-H-792 humidity cabinet test, salt spray test, fog cabinet test and others, these tests are quite often the basis for claims of effective corrosion control materials and methods. Lack of correlation with field tests seems to be the major deficiency of most accelerated tests, and poor reproducibility of results is another difficulty in many tests.

In order that the information developed in this research program might bear a more direct relationship to field tests, it seemed that an improved method of testing should be one of the aims of this program. The controlled cyclic condensation humidity cabinet developed by the Aeronautical Materials Laboratory of Naval Aeronautical Materials Center, Philadelphia appears to offer a significantly improved tool for use in research programs such as this project. There has been some success reported in achieving qualitative correlation with field tests and accelerated laboratory tests operated in a manner similar to the operation cycle of the controlled cyclic condensation humidity cabinet. However, the controlled cyclic condensation humidity cabinet appears to offer greater flexibility and economy of operation and construction.

A survey of corrosion literature indicates that there are currently no effective corrosion preventive compounds which function as ultra-thin films applied from dilute solutions.

Many materials are said to function as corrosion inhibitors by being adsorbed on metal surfaces in ultra-thin films (sometimes of molecular dimensions) in fluid or enclosed atmospheric environments. However, the literature is devoid of any mention of these materials being effective inhibitors, either as the sole film-former or as a component of an ultra-thin film applied from solution.

FUTURE WORK

All candidate films will first be evaluated for efficiency of corrosion inhibition by testing steel specimens in the controlled cyclic condensation humidity cabinet. Materials which appear to offer satisfactory protection to steel surfaces will be further tested on other metallic specimens (copper, brass, aluminum, etc.). Bimetallic specimens shall be tested in the cabinet to determine ability of films to prevent galvanic corrosion.

Extreme pressure properties and changes in extreme pressure properties shall be tested to reveal any tendency of the materials to interfere with lubricating properties.

Respectfully submitted,

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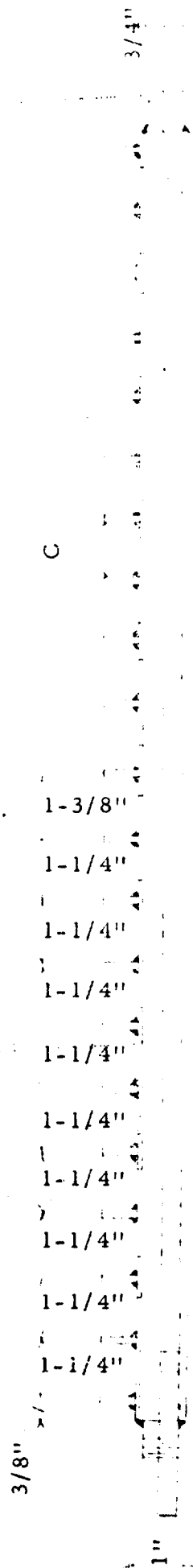
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CONTROLLED CYCLIC CONDENSATION HUMIDITY CABINET

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- Best Available Copy**